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TITLE: MANUFACTURE OF CONDUCTOR PASTE AND CERAMIC  
MULTILAYER SUBSTRATE

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ABSTRACT:

PROBLEM TO BE SOLVED: To manufacture a conductor paste, capable of obtaining a via conductor having a low resistance value, which does not generate defects such as voids or cracks and are superior in quality performance by the technology of a ceramic multilayer substrate and manufacture the ceramic multilayer substrate superior in quality performance by using the

conductor  
paste.

SOLUTION: A conductor paste 20, which contains a conductor powder made of Ag powder with the average grain size of 3-10  $\mu\text{m}$  at 95 wt.% of the overall conductor powder, an organic vehicle and no glass frit, is filled in via holes 12 of a green sheet 10, and heat contraction suppressing sheets 30 are laminated and baked on both faces of a green sheet layered product S to obtain a ceramic multilayer substrate. A drift rarely occurs in the sintering behavior between the green sheets 10 and the conductor paste 20.

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CLAIMS

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[Claim(s)]

[Claim 1] Conductive paste which does not contain a glass frit including the end of conducting powder Ag powder with a mean particle diameter of 3-10 micrometers consists of 95% of the weight or more of the whole in the end of conducting powder, and an organic vehicle.

[Claim 2] said conductor -- powder -- Pd powder with a mean particle diameter of 0.1-1 micrometer and/or Pt powder -- a conductor -- the conductive paste according to claim 1 which the whole powder contains 0.1 to 5% of the weight.

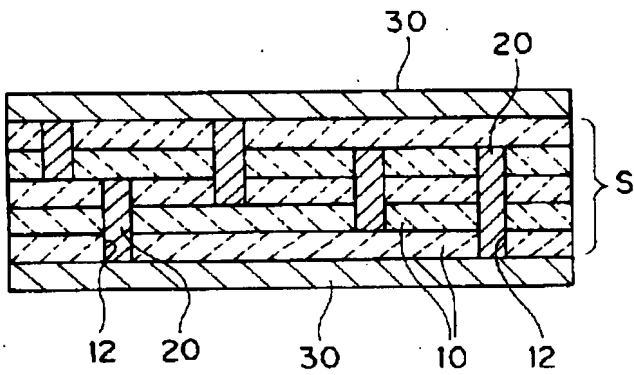
[Claim 3] The process which fills up with conductive paste according to claim 1 or 2 the beer hole which is the approach of carrying out two or more sheet laminating of the ceramic green sheet, calcinating it, and manufacturing a ceramic multilayer substrate, and was prepared in said green sheet, Carry out two or more sheet laminating of the green sheet with which it filled up with said conductive paste, and a heat shrink control sheet is arranged to the both sides. The manufacture approach of a ceramic multilayer substrate including the process which removes said heat shrink control sheet and obtains a ceramic multilayer substrate after calcinating the process which obtains the laminated material for baking, and the green sheet and conductive paste of said laminated material for baking.

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Drawing selection Representative drawing ▼

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the conductive paste used as the manufacture approach of the ceramic multilayer substrate used for manufacture of a high density wiring circuit plate, and a conductor material of such a wiring circuit plate.

[0002]

[Description of the Prior Art] The method of obtaining the ceramic multilayer substrate with which the multilayer circuit was formed by carrying out two or more sheet laminating of the ceramic green sheet with which the wiring circuit pattern was produced, and calcinating it as a manufacturing technology of a high density wiring circuit plate, is learned. In order to connect the circuits of each class of a ceramic multilayer substrate, in case a detailed through tube, i.e., a beer hole, is beforehand formed in the green sheet which constitutes each class, this beer hole is filled up with conductive paste and the layered product of a green sheet is calcinated, the circuit of each class is connected by calcinating to coincidence the conductive paste with which the beer hole was filled up.

[0003] As conductive paste for beer holes, the paste-like constituent with which a glass frit, binder resin, etc. were blended with the powder of conductive ingredients, such as Ag and Pd, is used. The technique of calcinating where the laminating of the heat shrink control sheet which controls the heat shrink of a layered product to both sides of a layered product is carried out as the baking approach of a green sheet layered product is proposed. The green sheet of the ceramic ingredient which does not cause a heat shrink, without sintering a heat shrink control sheet in the burning-temperature range of a green sheet layered product is used. By the laminating of the heat shrink control sheet which does not carry out a heat shrink being carried out, the heat shrink of a green sheet layered product is suppressed. Specifically, an alumina green sheet is used as a heat shrink control sheet to the layered product of a glass ceramic green sheet.

[0004]

[Problem(s) to be Solved by the Invention] the time of calcinating the green sheet layered product with which conductive paste was filled up into the beer hole, and manufacturing a ceramic multilayer substrate -- beer -- that an opening is made in the interior of a conductor \*\*\*\* -- beer -- the problem that a crack is made at the surrounding substrate of a conductor may occur Moreover, it may become high far rather than the value beer resistance is predicted to be. the beer of the part where said heat shrink control sheet carried out touches -- a conductor -- the mineral constituent contained on a heat shrink control sheet in a front face -- adhering -- beer -- a conductor -- another conductor on a front face -- when it was going to connect a circuit, the problem that connection dependability was spoiled remarkably was also generated.

[0005] It is thought that the cause which these problems produce has a big cause in gap of the sintering timing of the conductive paste and the glee sheet layered product with which the beer hole was filled up, or heat shrink behavior in a baking process. the substrate calcinated since big gap was in sintering with a green sheet layered product and the conductive paste of a beer hole, and beer -- excessive stress and

distortion arise between conductors and said generating of an opening or a crack carried out, increase of resistance, the fall of connection dependability, etc. arise in it.

[0006] although aiming at said solution in question solved was performed by changing various presentation combination of the conductive paste with which a beer hole is filled up -- so much -- coming out -- sufficient result was not obtained. Although it was thought that the above mentioned glass frit was an ingredient effective in adjusting the sintering property of conductive paste, even if it increased the loadings of a glass frit, said problem has not improved. When the heat shrink control sheet especially described above was used, it was not able to respond in conventional conductive paste.

[0007] the technical problem of this invention -- the beer of said ceramic multilayer substrate carried out -- the beer which canceled the trouble generated in a conductor and was excellent in electric and a mechanical property -- it is manufacturing the ceramic multilayer substrate which offered the conductive paste which can constitute a conductor and was excellent in the quality engine performance using such conductive paste.

[0008]

[Means for Solving the Problem] - the conductive paste concerning conductive paste-this invention -- Ag powder with a mean particle diameter of 3-10 micrometers -- a conductor -- the conductor which consists of 95% of the weight or more of the whole powder -- a glass frit is not included including powder and an organic vehicle.

[ -- a conductor -- powder] -- the beer after baking -- it is the component which achieves an electric conduction function in a conductor, and a metal or alloy powder excellent in conductivity is used.

[0009] Ag powder is made into the subject the conducting powder end of this invention, and 95% of the weight or more of the whole is Ag powder in the end of conducting powder. As for Ag powder, a thing with a mean particle diameter of 3-10 micrometers is used. With differences in particle size, the behavior at the time of baking changes greatly. even if a mean diameter is too small and it is too large -- beer -- it becomes easy to generate an opening and a crack in a conductor. if particle size is too small -- the time of baking -- beer -- a conductor -- a green sheet -- early -- contracting -- beer -- a conductor pulls a green sheet and a crack arises in the substrate of the beer hole circumference. if particle size is too large -- beer -- in order that sintering of a conductor may be overdue compared with a substrate -- beer -- an opening is generated between a conductor and a substrate. moreover, Ag powder whose particle size is too large -- beer -- the resistance of a conductor becomes large.

[0010] Another ingredient can be blended in the range which does not check the property which was excellent in Ag powder other than Ag powder in the end of conducting powder. Specifically, Pd powder and Pt powder can be used. Pd powder and Pt powder have the effectiveness which controls sintering of Ag powder. conductors other than Ag powder -- a powdered particle size -- beer -- effect arises for the engine performance of a conductor, it is comparatively alike, and the thing of a small particle size is desirable. Specifically, in the case of Pd powder or Pt powder, a thing with a mean particle diameter of 0.1-1 micrometer is desirable. When that whose particle size is too small has little effectiveness which controls sintering of Ag powder and particle size is too large, sintering of Ag powder will be controlled too much.

[Other components] The add-in material other than the end of conducting powder, such as glass and resin, is added to usual conductive paste, and the conductive paste of this invention can also blend the same add-in material as usual conductive paste with it fundamentally.

[0011] However, about a glass frit, it does not include in conductive paste. In order to make easy handling, such as restoration to the beer hole in the end of conducting powder, it is necessary to change into the so-called paste condition, therefore an organic vehicle needs to be blended. As an ingredient of an organic vehicle, the same ingredient as usual conductive paste is used. For example, ethyl cellulose etc. is mentioned.

[0012] The general blending ratio of coal can be used for the rate of the end of conducting powder and the organic vehicle in conductive paste. For example, an end:of conducting powder organic vehicle = 80:20 to about 95:5 are adopted.

- The manufacture approach of the ceramic multilayer substrate concerning manufacture-this invention

of a ceramic multilayer substrate is an approach of carrying out two or more sheet laminating of the ceramic green sheet, calcinating it, and manufacturing a ceramic multilayer substrate, and includes the following process.

[0013] The process which fills up with said conductive paste the beer hole prepared in the green sheet. The process which carries out two or more sheet laminating of the green sheet with which it filled up with conductive paste, arranges a heat shrink control sheet to the both sides, and obtains the laminated material for baking. The process which removes a heat shrink control sheet and obtains a ceramic multilayer substrate after calcinating the green sheet and conductive paste of the laminated material for baking.

[Ceramic green sheet] The ceramic green sheet used for manufacture of the usual ceramic multilayer substrate can be used. An alumina, crystallized glass, etc. are used as a ceramic ingredient.

[0014] Penetration formation of the beer hole is carried out at a green sheet. The dimension configuration of a beer hole is the same as that of the case of the usual multilayer substrate, and is good, and the arrangement pattern of a beer hole is decided by the circuit design. The path of a beer hole is usually about 0.1-0.3mm.

[Conductive paste restoration] The beer hole of a green sheet is filled up with the conductive paste of above mentioned this invention. The restoration approach is the same as that of manufacture of the usual circuit board, and is good.

[0015] A wiring circuit pattern is produced by the front face of a green sheet if needed. As for the method of producing a wiring circuit pattern, the usual circuit formation techniques, such as print processes, are applied. a wiring circuit pattern -- a conductor -- not only a circuit but functional divisions, such as resistance, can be included. A wiring circuit pattern is connectable with the conductive paste with which the above mentioned beer hole was filled up.

[Green sheet laminating] The laminating only of the required number of sheets is carried out, and a green sheet makes it a layered product. The laminating number of sheets of a green sheet can be set up suitably if needed, for example, is set up in several sheets to dozens of sheets.

[0016] Although it can also calcinate with this green sheet layered product, it is desirable to use a heat shrink control sheet. It is the sheet material which has the function which controls that a heat shrink control sheet causes a heat shrink with a superfluous green sheet when a green sheet layered product is calcinated. In the burning-temperature range of a green sheet layered product, an ingredient with a low coefficient of thermal expansion is used compared with a green sheet. For example, in the case of the green sheet which consists of crystallized glass comparatively calcinated at low temperature, in the burning-temperature range of crystallized glass, the green sheet which consists of an alumina ceramic which hardly produces thermal expansion can be used. A heat shrink control sheet is removed and removed from a ceramic multilayer substrate after a baking process.

[0017] A protection film can be arranged on both sides of a green sheet layered product, or the external surface of a heat shrink control sheet. In case [ which the green sheet layered product was transported to the pressurization process from the laminating process, or kept it temporarily ] I result, a protection film is used in order to protect a comparatively soft green sheet. What a protection film becomes from synthetic resin, such as PPS and PET, is used. A protection film is stuck during the handling from a temporary pressurization process to a pressurization process at a layered product, and achieves a protection feature.

[Baking of a green sheet and conductive paste] The same process as baking of the usual ceramic multilayer substrate is adopted. Burning temperature and firing time are set up according to the ingredient and military requirement of a green sheet.

[0018] When the laminating of the heat shrink control sheet is carried out to both sides of a green sheet layered product, the heat shrink of the green sheet in a baking process will be controlled with the heat shrink control sheet arranged to both sides. As for the ceramic multilayer substrate which finished the baking process and was obtained, post processing is performed if needed. For example, producing a wiring circuit pattern on the front face of a ceramic multilayer substrate, mounting an electronic device, or combining a ceramic multilayer substrate with another electronic parts is performed.

[0019]

[Embodiment of the Invention] The operation gestalt shown in drawing 1 expresses the structure of the gradual layered product which performs a baking process. A green sheet 10 prepares the slurry of a glass ceramic ingredient, and is fabricated in the shape of a sheet. At the green sheet 10, penetration formation of the beer hole 12 is carried out by punching processing etc. at the position.

[0020] The laminating of the green sheet 10 of two or more sheets is carried out, and it serves as the green sheet layered product S. The part which beer hole 12 comrades which it has in two or more green sheets 10 are opening for free passage is also produced. The interior of the beer hole 12 is filled up with conductive paste 20. The activity which fills up with conductive paste 20 the beer hole 12 which carries out opening to a front face may be repeated filling up the beer hole 12 with conductive paste 20 each green sheet 10 of every, and carrying out the laminating of the green sheet 10 one by one. Screen printing is applicable to restoration of conductive paste 20.

[0021] Although illustration is omitted, a wiring circuit pattern can be formed in the front face of a green sheet 10. A wiring circuit pattern can form the conductive paste 20 for beer holes, and the same conductive paste by screen-stencil. By screen-stencil, conductive paste 20 restoration of the beer hole 12 and surface circuit formation can also be performed to coincidence. Of course, the conductive paste suitable for formation of the surface circuit where presentation combination differs can also be used in the conductive paste 20 for beer holes.

[0022] The heat shrink control sheets 30 and 30 which become both sides of the green sheet layered product S from an alumina green sheet are arranged. It sends into the heating furnace for baking, and calcinates by heating the laminated material of this green sheet layered product S and the heat shrink control sheet 30 to the proper temperature around 1000 degrees C. A green sheet 10 and conductive paste 20 cause a heat shrink with sintering.

[0023] If a baking process is completed, the ceramic multilayer substrate which is the baking object of the green sheet layered product S will be obtained. What is necessary is for the heat shrink control sheet 30 to exfoliate from a ceramic multilayer substrate, and just to remove it.

[0024]

[Example] [Conductive paste] The conductive paste of presentation combination shown in the following table 1 was manufactured, and the engine performance was evaluated. Ag which specifically has specific mean particle diameter -- independent or the conductor which consists of Ag and Pd -- it is carrying out 5-25 weight section addition of what dissolved ethyl cellulose by terpineol to the powder 100 weight section, using 3 roll equipment, and fully mixing and kneading, and conductive paste was obtained.

[0025] The "glass addition" in Table 1 expresses the addition of a glass frit (the mean particle diameter of 1.5-2.0 micrometers, the glass transition point of 670 degrees C, crystallization temperature of 980 degrees C).

[Green sheet] The glass ceramic green sheet which uses boric acid lead silicate glass and an alumina as a principal component was used.

[0026] The beer hole of 0.2mmphi was processed into the green sheet. The beer hole of a green sheet was filled up with said conductive paste. Moreover, the conductive paste for inner layer circuits which uses Ag as a principal component was printed by screen-stencil on the surface of the green sheet, and the inner layer circuit pattern was formed. After performing the same processing as the green sheet of two or more sheets, the laminating was carried out, and the green sheet layered product was obtained.

[0027] The heat shrink control sheet which becomes both sides of a green sheet layered product from an alumina green sheet was piled up. The sintering temperature of an alumina green sheet is 1300-1500 degrees C, and is fully higher than a glass ceramic green sheet. The laminating unification of a green sheet layered product and the heat shrink control sheet was carried out at 80-100 degrees C, having put the pressure of 100-200kg/cm<sup>2</sup>.

[0028] This laminated material was calcinated over 10 - 15 minutes at 900 degrees C, after heating and degreasing at 400-700 degrees C. As for the obtained ceramic multilayer substrate, contraction of the direction of a flat surface was controlled good in the operation of a heat shrink control sheet. The result of having analyzed and evaluated the obtained ceramic multilayer substrate is shown in Table 1.



[0029] the inside of evaluation criteria, and "beer resistance" -- beer -- the resistance per piece of a conductor is shown. "an opening and a crack" -- beer -- the existence of the opening produced between a conductor, a beer hole, or a wiring circuit or the crack produced in a substrate was observed. "adhesion of fine particles" -- the surface part of a ceramic multilayer substrate -- it is -- beer -- it observed whether the alumina powder which is the ingredient of a heat shrink control sheet would have adhered on the surface of a conductor.

[0030]

[Table 1]

----- The presentation in the end of conducting powder Glass Beer Opening -  
 Fine particles Weight % (particle-size mum) Addition Resistance Crack Adhesion Ag Pd Weight %  
 mohms Existence existence ----- example 1 99 (3) 1 (1.0) 0 0.8 Nothing Nothing  
 Example 299 (5) 1 (0.5) 0 0.9 Nothing Nothing Example 3 99 (10) 1 (0.1) 0 1.0 Nothing Nothing  
 Example 4 95 (3) 5 (0.5) 0 1.0-less \*\*\*\* Example 5 95(5) 5 (1.0) 0 1.5 Nothing Nothing Example 6 100  
 (10) - 0 1.5 Nothing nothing ----- Example 1 of comparison 95 (1) 5 (1.0) 0 1.0  
 \*\*\*\* Nothing Example 2 of a comparison 100 (15) - 0 5 It is. It is. Example 3 of a comparison 70 (1) -  
 30 20 It is. Nothing Example 4 of a comparison 80 (5) 5 (1.0) 20 20 \*\*\*\* It is. Example 5 of a  
 comparison 90 (10) - 10 15 it is -- \*\*\*\* ----- the above result -- the example of  
 this invention -- beer -- the beer which is low as for the resistance of a conductor, and generating of an  
 opening or a crack does not have, either, and did not produce adhesion of alumina powder, either, but  
 was equipped with the outstanding property -- the ceramic multilayer substrate which has a conductor is  
 obtained. If an example 6 and an example 3 are contrasted, beer resistance is falling by blending little Pd  
 with Ag, and the usefulness of blending Pd is also proved.

[0031] On the other hand, in the examples 1 and 3 of a comparison, since the particle size of Ag is small,  
 the opening and the crack have occurred. In the example 2 of a comparison, while the particle size of Ag  
 is large and resistance is increasing, the opening and the crack occurred and adhesion of alumina powder  
 is also produced. In the examples 3-5 of a comparison, by having blended the glass frit, resistance  
 became very large and has also produced adhesion of an opening and alumina powder.

[0032]

[Effect of the Invention] The manufacture approach of the conductive paste concerning this invention  
 and a ceramic multilayer substrate is that a glass frit is not included while the conducting powder end of  
 conductive paste makes Ag powder of a specific particle size the subject, and when a ceramic multilayer  
 substrate is calcinated, big gap does not produce it in sintering with conductive paste and a green sheet.  
 consequently, the calcinated ceramic multilayer substrate -- beer -- it is hard to produce an opening  
 between a conductor and a substrate, that a crack occurs in a substrate also decreases, and it becomes  
 what was excellent also in electrical characteristics, such as resistance.

[0033] beer [ in / when it calcinates especially by using a heat shrink control sheet at the time of baking,  
 and controlling the heat shrink of a green sheet layered product, sintering with a green sheet and  
 conductive paste can be performed good, and / a ceramic multilayer substrate ] -- it becomes the thing  
 excellent in the property of a conductor etc.

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[Translation done.]